

Enhanced annealing effect in an oxygen atmosphere on $\text{Ga}_{1-x}\text{Mn}_x\text{As}$

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We report on in-situ resistivity measurements on $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ during post-growth annealing in different atmospheres. A drop in the resistivity is observed when the $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ is exposed to oxygen, which indicates that the passivation of Mn interstitials (Mn_I) at the free surface occurs through oxidation. The presence of oxygen can therefore be an important annealing condition for the optimization of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ thin films, all the more since the oxidation appears to be limited to the sample surface. Annealing in an oxygen-free atmosphere leads to an increase in the resistivity indicating a second annealing mechanism besides the out-diffusion of Mn_I . According to our magnetization and Hall effect data, this mechanism reduces the amount of magnetically and electrically active Mn atoms.

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The combination of ferromagnetism with the versatile semiconducting properties in III-V ferromagnetic semiconductors such as $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ makes them promising for future spintronics applications, in which the spin degree of freedom is used to process and transfer information. The amount of Mn, that has to be incorporated to obtain ferromagnetic $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ epilayers, is far above the equilibrium solubility limit. Therefore these films have to be grown at low temperatures using molecular beam epitaxy (MBE) [1]. When Mn ions are incorporated into GaAs, they do not only introduce magnetic moments but also act as acceptors, providing holes that mediate the interaction between the localized Mn spins. Obtaining higher values for the Curie temperature T_C is therefore not only a matter of increasing the Mn content, but also of achieving a higher free carrier density. The low growth temperatures, however, lead to a high density of Mn interstitials (Mn_I) and As antisite defects (As_Ga) which both act as double donors [2, 3, 4], and therefore compensate a fraction of the holes generated by the substitutional Mn_Ga acceptor. Several authors have reported an enhancement of the hole concentration and T_C upon after growth annealing at temperatures close to the growth temperature [5, 6, 7, 8, 9, 10, 11, 12]. The best results so far were obtained for annealing temperatures T_A just below the growth temperature [9, 12], while long annealing times and higher temperatures result in a reduction of T_C [5, 6, 7, 8, 13]. The optimization of T_C can be done in a controlled way by monitoring the resistance while annealing [9], as the high temperature resistivity is correlated with the hole concentration, and therefore with T_C . From ion channeling experiments Yu et al. showed strong evidence that this increase of T_C is related to the removal of Mn_I atoms [14], while Edmonds et al. recently identified the underlying mechanism with the outdiffusion of the highly mobile Mn_I to the free surface [15]. It was already suggested by Edmonds et al. that at the surface the interstitial Mn atoms may be pas-

sivated by oxidation [15]. This mechanism is supported by the capping-induced suppression of the annealing effects [11, 16]. In this paper we present evidence that the presence of oxygen is an important parameter for the optimization of T_C through annealing, indicating that the passivation of Mn_I indeed occurs through oxidation.

$\text{Ga}_{1-x}\text{Mn}_x\text{As}$ films with various Mn content ($0.03 \leq x \leq 0.08$) were deposited by standard low-temperature molecular beam epitaxy on semi-insulating epi-ready (001) GaAs substrates. The growth was performed with a nearly stoichiometric As_2 flux at temperatures typically $\approx 15^\circ\text{C}$ below the Mn segregation limit, on a 100 nm high-temperature GaAs buffer layer grown under standard conditions, followed by a low temperature GaAs buffer of a similar thickness. The growth was monitored in situ by reflection high energy electron diffraction (RHEED), which showed a clear (1×2) reconstruction. The structural quality and the sample thickness of about 40 nm were checked with XRD measurements. A part of the wafer was then chemically etched into Hall bars using photo-lithography. A small variation of about 3% in the room temperature resistivity was observed in samples that were taken from the same wafer. Post-growth annealing was performed in a tube furnace, which allows a well controlled atmosphere, consisting of vacuum or a specific gas, for the annealing procedure. The resistance was measured in-situ in a four probe configuration. Magnetization measurements were performed with vibrating sample magnetometer (VSM) on unprocessed samples with a typical size $\sim 30 \text{ mm}^2$.

To investigate the role of oxygen in the annealing process, we have subjected the samples to an after-growth annealing procedure in which the atmosphere was initially oxygen-free and after a well defined annealing time the epilayers were exposed to oxygen. To ensure the oxygen-free initial atmosphere, the quartz tube containing the sample was pumped to a vacuum of the order of 10^{-6} mbar, flushed out and filled with forming gas con-

sisting of 99% N₂ gas and 1% H₂ gas. The tube was then sealed, while filled with forming gas at a slight overpressure (≈ 0.1 bar). Within about 20 minutes the annealing temperature is stabilized with little overshoot ($\leq 1^\circ\text{C}$). After a well controlled time, the tube containing the sample is exposed to a gentle O₂ gas flow, typically for 5 to 10 minutes, maintaining a constant temperature and ensuring an oxygen pressure of the order of 1 bar. During this entire procedure the resistance is continuously monitored. Fig. 1 shows the resistivity as a function of time for Ga_{1-x}Mn_xAs ($x = 0.06$) at 159°C, 177°C and 201°C. The resistivity initially decreases with a rate that diminishes with time (note that the time in Fig. 1 is plotted on a logarithmic scale), and then rises again for $T_A = 177^\circ\text{C}$ and 201°C , which will be discussed later. Upon exposure to oxygen a sudden resistivity drop occurs, which is very sharp for $T_A = 201^\circ\text{C}$, and shows diffusion-like behavior similar to that reported by Edmonds et al. [9, 15]. A similar drop in resistivity occurs when N₂ gas is used as initial atmosphere or for samples with a different Mn content. These results clearly show that the presence of oxygen enhances the resistivity reduction upon annealing, which corroborates the migration of hole-compensating interstitials to the free surface during the annealing process [15], where they are passivated through oxidation. This reduction of compensating defects results in the observed increase in hole density and conductivity. The Ga_{1-x}Mn_xAs epilayer itself does not appear to suffer from oxidation, since this would lead to an increase in the resistivity. This is confirmed by low angle XRD measurements on a 235 nm Ga_{1-x}Mn_xAs ($x = 0.07$) film, which indicate a natural oxide layer with a thickness of 2 nm, while after annealing in O₂ gas ($\approx 200^\circ\text{C}$, 80 hours) this thickness only increased to about 5 nm.

Fig. 2 shows the resistivity versus temperature for a sample with $x = 0.06$, both as-grown (curve a) and after annealing at $\approx 200^\circ\text{C}$ for 60 hours in an O₂ atmosphere (curve c). Both curves show typical behavior for metallic Ga_{1-x}Mn_xAs, with a peak at $T_p = 82$ K for the as-grown sample, and $T_p = 162$ K for the oxygen-annealed one. The peak temperature gives a good estimate of the Curie temperature for the as grown sample. The direct measurement of T_C with vibrating sample magnetometry gives $T_C = 81$ K. However, for the annealed sample T_p is found to overestimate the measured $T_C = 133$ K by 29 K, which is a large deviation, even considering the broadness of the resistivity peak.

To investigate further the increase in resistivity observed at $T_A = 177^\circ\text{C}$ and 201°C (before exposure to O₂), the same annealing procedure was repeated without oxygen, thus in a forming gas atmosphere. The resistivity of Ga_{1-x}Mn_xAs ($x = 0.07$) as a function of time at 198°C is shown in Fig. 3. The resistivity initially drops, but then quickly increases with a rate that decreases with time. A similar effect is observed for samples with various Mn content and the slowly increasing resistivity was established for annealing times exceeding 100 hours. It is unlikely that the increase in resistivity is caused by

the passivation of the Ga_{1-x}Mn_xAs layer due to hydro-generation as described recently by Brandt et al. [17], as a similar resistivity curve was observed when annealing in a N₂ gas atmosphere and in vacuum. The resistivity increase is even observed at $T_A = 158^\circ\text{C}$ when annealing Ga_{1-x}Mn_xAs ($x = 0.04$ and $x = 0.08$) in vacuum, albeit only by about 20% after annealing for 120 hours. These results are in agreement with the increased resistance observed for long annealing times and higher temperatures [5, 6, 7, 8, 13]. The resistivity versus temperature for Ga_{1-x}Mn_xAs ($x = 0.06$) after annealing in forming gas is plotted in fig. 2 as curve (b) and shows semiconducting behavior with a slight deviation around 25 K. To determine the carrier type and concentration, Hall effect measurements in DC magnetic fields up to 12 T were performed at 300K, which is far above T_C so no significant paramagnetic contribution through the anomalous Hall effect was detected. The Hall data revealed positive holes as carriers with a concentration of $4.6 \times 10^{19} \text{ cm}^{-3}$ for Ga_{1-x}Mn_xAs ($x = 0.06$) annealed in forming gas, which is almost an order of magnitude less than the hole concentration $p = 2.0 \times 10^{20} \text{ cm}^{-3}$ found for the as-grown sample from Hall measurements at 5 K. The latter value for p was obtained by taking the magnetoresistance contribution to the anomalous Hall effect into account, by assuming the anomalous Hall coefficient $R_A \propto \rho^2$.

Magnetization measurements performed on Ga_{1-x}Mn_xAs ($x = 0.07$) show that the easy axes for as-grown samples are [100] and [010] in-plane, while after a similar annealing treatment in forming gas the easy axis is shifted to the out-of-plane [001] axis, as expected for Ga_{1-x}Mn_xAs with such a low hole concentration [18, 19]. When measuring along the easy axis, the magnetic moment shows no significant increase when the magnetic field is raised from 20 mT to 0.5 T, indicating that the samples are in a nearly single domain state at remanence. Macroscopic single domains in Ga_{1-x}Mn_xAs have been established with scanning SQUID microscopy [20], scanning Hall probe microscopy [21] and planar Hall effect measurements [22]. Therefore the remanent magnetization M_{rem} along the easy axis is a good measure of the saturation magnetization of the Ga_{1-x}Mn_xAs layer. As can be seen from the inset of Fig. 3, M_{rem} has decreased by more than 50 % as a consequence of the annealing procedure.

These results show that there is a second mechanism besides the diffusion of Mn_I. This mechanism appears to diminish the amount of ferromagnetically coupled Mn ions, as M_{rem} has decreased, and since the carrier concentration is strongly reduced, this may be due to the removal of Mn from electrically active Ga sites. The fact that the remaining carriers are still found to be p-type indicates that Mn_{Ga} ions do not simply move to interstitial positions, as an excess of Mn_I would lead to electrons as carriers. The activation energy for the removal of Mn_{Ga} will be much higher than that for the out-diffusion of Mn_I, which therefore dominates in an O₂ atmosphere. When no oxygen is available, no passivation at the sur-

face can occur, but the relatively mobile Mn_I are still free to migrate through the epilayer. An additional mechanism could be the formation of Mn-As complexes, possibly with Mn_I as an intermediate state. MnAs inclusions were previously observed after annealing at high temperatures (600°C) [23]. The initial decrease in resistivity upon annealing as seen in Fig. 1 and 3 may be due to the passivation of some Mn_I at the natural oxide layer at the sample surface and the limited diffusion of Mn_I to the substrate.

In summary, exposure of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ to oxygen during annealing causes a substantial drop in the resistivity, which indicates that the passivation of Mn_I at the free surface occurs through oxidation. The presence of oxygen can therefore be an important post-growth annealing condition for the optimization of this system. Annealing in an oxygen-free atmosphere leads to an increase in the

resistivity indicating a second annealing mechanism besides the out-diffusion of Mn_I , that reduces the amount of electrically and magnetically active Mn atoms.

Acknowledgments

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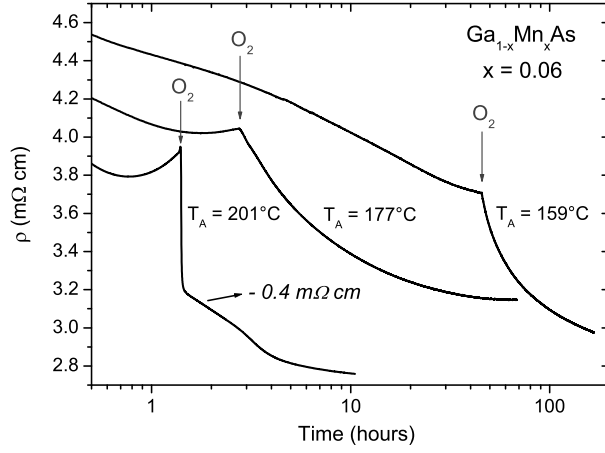


FIG. 1: Resistivity versus annealing time for 40 nm thick $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ ($x = 0.06$) films at 159°C , 177°C and 201°C , measured in a four probe configuration. The annealing is initially performed in a forming gas atmosphere ($\text{N}_2 + 1\% \text{H}_2$). The arrows indicate when the samples were exposed to oxygen. The curve at 201°C is shifted by $-0.4 \text{ m}\Omega \text{ cm}$ for clarity.

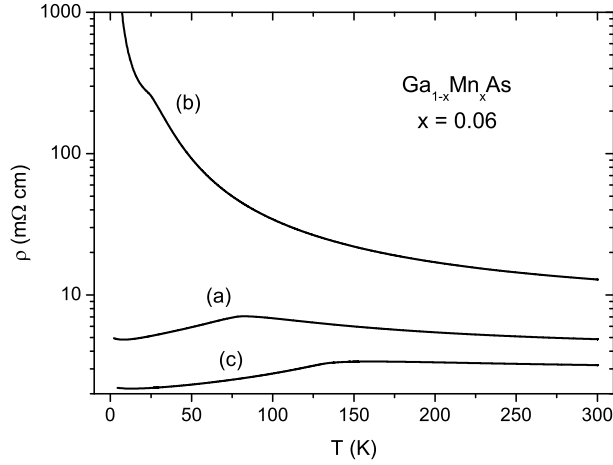


FIG. 2: Temperature dependence of the resistivity of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ ($x = 0.06$) films (a) as-grown, (b) after annealing with only forming gas (198°C , 16 hours), (c) after annealing in an oxygen atmosphere (190°C , 70 hours).

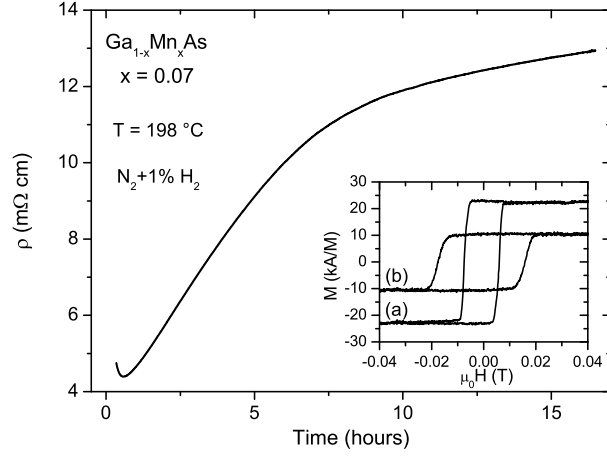


FIG. 3: Resistivity versus annealing time for a $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ ($x = 0.07$) film in a forming gas atmosphere at 198°C . The inset shows hysteresis loops measured at 5 K for $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ ($x = 0.07$): (a) as-grown, measured along the $[100]$ easy axis; (b) after annealing in a forming gas atmosphere (199°C , 25 hours), measured along the $[001]$ easy axis.